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PREPARATION AND STRUCTURE OF A SIXTEEN-MEMBERED RING WITH ALTERNATING CN AND SN GROUPS

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Abstract The reaction of trisilylated benzamidines $\text{ArCN}_2(\text{SiMe}_3)_3$ with PhSCl in a 1:3 molar ratio produces cyclic compounds of the type $(\text{ArCNS}(\text{Ph})\text{N})_n$ ($n=2, 4$) in addition the diazenes *trans*- $\text{PhSNC}(\text{Ar})\text{N}=\text{NC}(\text{Ar})\text{NSPh}$. The X-ray structure of the sixteen-membered ring $(4\text{-BrC}_6\text{H}_4)_4\text{C}_4\text{N}_8\text{S}_4\text{Ph}_4$ has been determined.

INTRODUCTION

The reaction of trisilylated benzamidines $\text{ArCN}_2(\text{SiMe}_3)_3$ with PhSCl in a 1:3 molar ratio provides a source of both cyclic and acyclic compounds with SNCN frameworks.^{1,2} When $\text{Ar}=\text{Ph}$ the major product is the purple diazene *trans*- $\text{PhSNC}(\text{Ar})\text{N}=\text{NC}(\text{Ar})\text{NSPh}$. The introduction of a *para*- CF_3 substituent on the aryl group attached to carbon results in the formation of cyclic oligomers in addition to the diazene and the eight-membered ring $(4\text{-F}_3\text{CC}_6\text{H}_4)_2\text{C}_2\text{N}_4\text{S}_2\text{Ph}_2$ has been isolated and characterized by spectroscopic methods and solution molecular weight determination. In this contribution the isolation and X-ray structure of the novel sixteen-membered ring $(4\text{-BrC}_6\text{H}_4)_4\text{C}_4\text{N}_8\text{S}_4\text{Ph}_4$ is described.

REACTION OF $(4\text{-BrC}_6\text{H}_4)\text{CN}_2(\text{SiMe}_3)_3$ WITH PHENYLSULFENYL CHLORIDE

The reaction of $\text{ArCN}_2(\text{SiMe}_3)_3$ ($\text{Ar}=4\text{-BrC}_6\text{H}_4$) with PhSCl in a 1:3 molar ratio was carried out in CH_2Cl_2 at -78°C . A TLC of the reaction mixture revealed a variety of products in addition to the purple diazene *trans*- $\text{PhSNC}(\text{Ar})\text{N}=\text{NC}(\text{Ar})\text{NSPh}$ and Ph_2S_2 . Subsequent work-up led to the isolation of the eight-membered ring $(4\text{-BrC}_6\text{H}_4)_2\text{C}_2\text{N}_4\text{S}_2\text{Ph}_2$, which was identified by FAB mass spectroscopy and a preliminary X-ray structure, and very low yields of the novel sixteen-membered ring $(4\text{-BrC}_6\text{H}_4)_4\text{C}_4\text{N}_8\text{S}_4\text{Ph}_4$ whose structure is described below.

X-RAY STRUCTURE OF (4-BrC₆H₄)₄C₄N₈S₄Ph₄ (1)

Two views of the unique macrocycle **1** are shown in Figure 1. The sixteen-membered C₄N₈S₄ ring is composed of alternating CN and SN groups and adopts a cradle-like structure with S₄ symmetry. The endocyclic bond lengths are: C(1)-N(1)=1.359(9), C(1)-N(2)=1.317(9), S(1)-N(1)=1.649(7), S(1)-N(2)=1.667(7) Å. The cavity formed by the four coplanar N(1) atoms is of the appropriate size to accommodate a K⁺ ion.

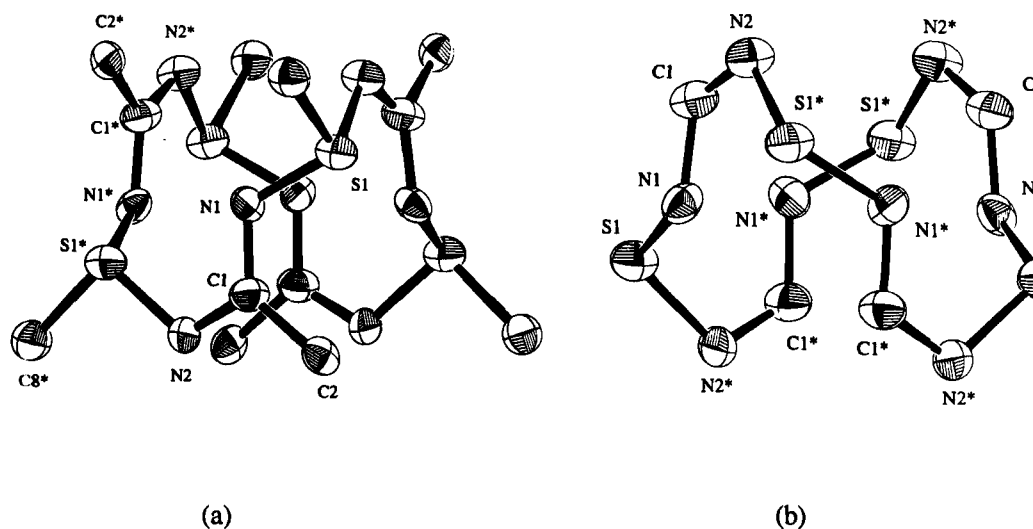


FIGURE 1 Two views of the C₄N₈S₄ ring in **1**. In (a) the α -carbon atoms of exocyclic substituents are shown. (Asterisks indicate symmetry related atoms).

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